Coordination Chemistry of a Chelating Amidoximato Ligand

Mikhail V. Barybin, Paula L. Diaconescu, and Christopher C. Cummins*

Department of Chemistry, Room 2-227, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139-4307

Received January 9, 2001

A potentially general strategy for accessing the rarely encountered coordination of amidoximates through both oximato O and amido N atoms was developed. The new amidoxime (*Z*)-$R^1C(=NOH)NR^2H$ (R^1 = mesityl, R^2 = 2-[{dimethylamino}methyl]phenyl), H_2L, was prepared by reaction of equimolar amounts of the appropriate nitrile oxide and primary amine. Treatment of H_2L with 1 equiv of $AlMe_3$ produced the dimeric species $(MeAlL)_2$ (**1**) possessing the formally dianionic ligand L^{2-} bound to the aluminum via the oximato oxygen and the amido and amino nitrogens. The oximato oxygen atoms serve to link the two monomeric organoaluminum units together. Reaction of $(ON)Cr(N^iPr_2)_3$ with H_2L provided the diamagnetic complex $(ON)Cr(N^iPr_2)(\eta^3\text{-L})$ (**2**). Interaction of **2** with excess methanol led, in particular, to the oxidative loss of NO and yielded the paramagnetic dimer $[Cr(LH)(OMe)(\mu\text{-OMe})]_2$ (**3**) containing the η^3-bound amidoximato ligand protonated at its oximato nitrogen. In addition to spectroscopic characterizations of the new substances, single-crystal X-ray structures of H_2L, $\mathbf{1}\cdot{}^4/_3C_6H_6$, and **3**·MeOH were obtained.

Introduction

Molecules containing the amidoxime functional group, $R^1C(=NOH)NR^2R^3$, have proven to be important reagents in organic synthesis.[1] Compounds of this type have found a variety of medicinal applications because of their biological activity.[2] In addition, amidoximes have been used for analytical determination of certain ions[1a,3] and for extraction of heavy metal cations from solutions over a wide pH range (e.g., extraction of uranium from seawater).[1a,4] Organometallic and coordination chemistries of oximes constitute an active area of research, with efforts in particular being directed toward unusual reactivity modes of oximes and their complexes.[1a,5,6] The vast majority of amidoxime organometallic systems contain late transition metals and exhibit bonding through the oxime nitrogen, as is also true of oxime complexes in general.[1a,3b,6−8] Ligation via oxime/oximato oxygen and amido nitrogen is far less common.[3b,6−9] Typically, the amido nitrogen is not involved in bonding with the metal, especially if the ligand contains additional functional groups capable of coordination.[8] While several metal complexes containing dianionic amidoximato functionality $[-ON=C(R^1)NH-]^{2-}$ bound through oximato oxygen and amido nitrogen atoms have been documented,[9] analogous N-substituted amidoximato ligands $[-ON=C(R^1)NR^2-]^{2-}$ ($R^2 \neq H$) have not been established. This work describes the generation of such units and their compatibility with various organometallic fragments.

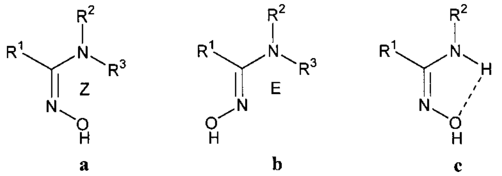


Figure 1. *Z* (a) and *E* (b) configurations of an amidoxime and hydrogen bonding within an N-monosubstituted *Z* amidoxime (c).

Depending on the nature of substitution at their amido nitrogen, amidoximes can adopt a *Z* or an *E* configuration (Figure 1a,b). Calculations at different levels have indicated that the *Z* form is more stable in the case of unsubstituted ($R^2 = R^3 = H$) and N-monosubstituted ($R^3 = H$) amidoximes.[2,10] X-ray structural and NMR spectroscopic investigations have shown that molecules $R^1C(=NOH)NH_2$ exist only as *Z* isomers. Compounds of the type $R^1C(=NOH)NHR^2$ possess a *Z* con-

---

* Corresponding author e-mail: ccummins@mit.edu.

(1) (a) Kukushkin, V. Y.; Tudela, D.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1996**, *156*, 333 and references therein. (b) Poplavskaya, I. A.; Kurmangaleeva, R. G. *Khimia Amidoximov* (*Chemistry of Amidoximes*); Nauka: Alma-Ata, 1988.

(2) Srivastava, R. M.; Brinn, I. M.; Machuca-Herrera, J. O.; Faria, H. B.; Carpenter, G. B.; Andrade, D.; Venkatesh, C. G.; de Morais, L. P. F. *J. Mol. Struct.* **1997**, *406*, 159 and references therein.

(3) (a) Jara, R.; Estela, J. M.; Cerda, V. *Thermochim. Acta* **1991**, *177*, 229. (b) Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 47 and references therein. (c) Rindorf, G. *Acta Chem. Scand.* **1971**, *25*, 774.

(4) (a) Saliba, R.; Gauthier, H.; Gauthier, R.; Petit-Ramel, M. *J. Appl. Polym. Sci.* **2000**, *75*, 1624 and references therein. (b) Choi, S. H.; Nho, Y. C. *Radiat. Phys. Chem.* **2000**, *57*, 187 and references therein. (c) Park, Y.-Y.; Kim, S.-Y.; Kim, J.-S.; Harada, M.; Tomiyasu, H.; Nogami, M.; Ikeda, Y. *J. Nucl. Sci. Technol.* **2000**, *37*, 344 and references threrein.

(5) Kukushkin, V. Y.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1999**, *181*, 147.

(6) Ganguly, S.; Karmakar, S.; Kumar Pal, C.; Chakravorty, A. *Inorg. Chem.* **1999**, *38*, 5984.

(7) (a) Gerasimchuk, N. N.; Bowman-James, K. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: Chichester, 1994; Vol. 5, pp 2254−2270. (b) Mehrotra, R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, pp 269−291.

(8) Selected recent examples: (a) Bovenzi, B. A.; Pearse, G. A. *J. Chem. Soc., Dalton Trans.* **1997**, *16*, 2793. (b) Pearse, G. A.; Raithby, P. R.; Maughan, M. M. J. *Polyhedron* **1996**, *13*, 553. (c) Werner, M.; Berner, J.; Jones, P. G. *Acta Crystallogr., Sect. C*: *Cryst. Struct. Commun.* **1996**, *52*, 72. (d) Razik, A. A.; Hadi, A. K. A. *Trans. Met. Chem.* **1994**, *19*, 84. (e) Pearse, G. A.; Pfluger, C. E. *Inorg. Chim. Acta* **1994**, *227*, 171. (f) Pearse, G. A.; Paithby, P. R.; Lewis, J. *Polyhedron* **1989**, *8*, 301.

(9) (a) Roh, S.-G.; Proust, A.; Robert, F.; Gouzerh, P. *J. Cluster Sci.* **1996**, *7*, 593. (b) Chilou, V.; Gouzerh, P.; Jeannin, Y.; Robert, F. *J. Chem. Soc., Chem. Commun.* **1989**, 76. (c) Saarinen, H.; Orama, M.; Korvenranta, J. *Acta Chem. Scand.* **1989**, *43*, 834. (d) Sletten, E.; Marthinsen, T.; Sletten, J. *Inorg. Chim. Acta* **1984**, *93*, 37. (e) Bellon, P. L.; Cenini, S.; Demartin, F.; Monassero, M.; Pizzotti, M.; Porta, F. *J. Chem. Soc., Dalton Trans.* **1980**, 2060.

10.1021/ic0100370 CCC: $20.00

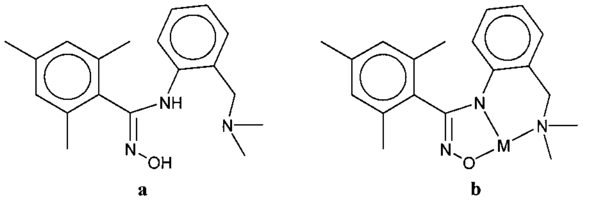
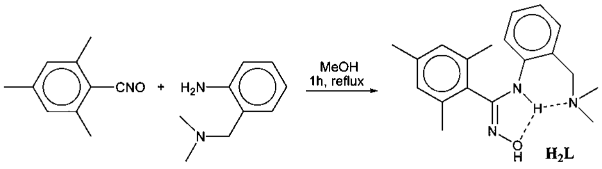


Figure 2. Amidoxime H_2L (a) and proposed coordination of L^{2-} to a metal center (b).

figuration in the solid state but often equilibrate in solution, with the *Z*−*E* isomerization barrier being about 20 kcal/mol.[11] The relative stability of the *Z* form is believed to be a consequence of intramolecular hydrogen bonding (Figure 1c) together with the fact that interaction of oxygen and amido nitrogen lone pairs should destabilize the *E* configuration.[10] Taking the foregoing information into account, we designed a new amidoxime H_2L (Figure 2a), incorporating a pendant amino functionality. Double deprotonation of this species was expected to lead to a dianionic chelating ligand capable of forming a five-membered ring upon binding to a metal center. In addition, such complexation was anticipated to be enhanced by coordination of the amino arm, providing a six-membered metallacycle (Figure 2b).

Results and Discussion

Synthesis and Characterization of the Amidoxime H_2L. A high-yield preparation of H_2L was accomplished by refluxing equimolar amounts of mesitylnitrile oxide and 2-[(dimethylamino)methyl]aniline in methanol (eq 1).[12] The latter reactants



(1)

are easily accessible from commercially available mesitaldehyde and 1-(chloromethyl)-2-nitrobenzene, respectively.[13]

The IR spectrum of H_2L in THF exhibits a very broad band at ca. 3350 cm^{-1}, corresponding to O−H and N−H stretching vibrations. The ν_{CN} energy of 1622 cm^{-1} is typical for aryl amidoximes.[14] The ^1H and ^{13}C NMR patterns for H_2L in C_6D_6, $CDCl_3$, or C_5D_5N solutions are consistent with the presence of only one (*Z*) isomer. Both NH and OH hydrogens resonate near 10.5 ppm, belying their acidic nature. X-ray crystallographic characterization of H_2L (Table 1, Figure 3) confirmed the *Z* configuration of the amidoxime and revealed intramolecular interactions of the NH hydrogen with oxygen (H(2)···O(1), 2.13 Å) and nitrogen of the NMe_2 group (H(2)···N(3), 2.19 Å). The amidoxime ONCN moiety is planar as evidenced by the dihedral O(1)−N(1)−C(1)−N(2) angle of 0.5(3)°. Steric repulsions within H_2L are minimized by rotation of the aryl fragments with respect to the amidoxime plane. The angles formed by the mesityl and C_6H_4 rings with the ONCN plane are ca. 95 and 35°, respectively, giving a 60° angle between the planes of the aryl groups. Similar features were observed for the structure of related N-phenyl-4-nitrobezamidoxime.[15] All bond distances and angles obtained for H_2L are well within their expected values.[16] Figure 3 illustrates clearly that, at least from a geometric point of view, H_2L is an excellent precursor for a tridentate, meridional, dianionic ligand L^{2-}.

Table 1. Crystal Data, Data Collection, Solution, and Refinement for H_2L, $\mathbf{1}\cdot{}^4/_3C_6H_6$, and $\mathbf{3}\cdot MeOH$

compound	H_2L	$\mathbf{1}\cdot{}^4/_3C_6H_6$	$\mathbf{3}\cdot MeOH$
empirical formula	$C_{19}H_{25}N_3O$	$C_{24}H_{30}AlN_3O$	$C_{22}H_{34}CrN_3O_4$
fw	311.42	403.49	452.49
cryst habit, color	plate, colorless	prizm, colorless	block, green
cryst size (mm)	0.19 × 0.14 × 0.08	0.14 × 0.13 × 0.10	0.17 × 0.10 × 0.06
cryst syst	triclinic	triclinic	orthorombic
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
a (Å)	8.9440(13)	13.106(2)	12.8446(13)
b (Å)	9.2460(14)	16.438(2)	15.318(2)
c (Å)	11.688(2)	17.577(3)	24.132(2)
α (deg)	79.151(3)	71.248(2)	90
β (deg)	79.863(3)	78.844(3)	90
γ (deg)	74.143(2)	83.178(3)	90
V (Å^3)	905.2(2)	3511.7(9)	4748.3(8)
Z	2	6	8
ρ_{calc} (mg m^{-3})	1.143	1.145	1.266
μ (mm^{-1})	0.072	0.105	0.512
F(000)	336	1296	1912
temp (K)	183(2)	183(2)	183(2)
θ range (deg)	2.32−23.27	2.06−23.28	2.23−20.25
index range	$-9 \le h \le 9$ $-10 \le k \le 10$ $-8 \le l \le 12$	$-14 \le h \le 13$ $-18 \le k \le 18$ $-18 \le l \le 29$	$-14 \le h \le 14$ $-17 \le k \le 13$ $-26 \le l \le 23$
rflns collected	3688	14461	13558
independent rflns	2553	9958	2303
R_{int}[a]	0.0437	0.1116	0.1095
max/min transm	0.4085/0.3177	0.4726/0.2909	0.2709/0.2232
data/restraints/params	2553/0/308	9958/0/784	2221/0/275
R1[b]; wR2[c]($I > 2\sigma(I)$)	0.0482; 0.1223	0.0827; 0.2192	0.0718; 0.1537
GOF on F^2	1.057	1.032	1.139
largest diff peak/hole (e Å^{-3})	0.214/−0.233	0.785/−0.394	0.329/−0.293

[a] $R_{int} = \sum|F_o^2 - \langle F_c^2\rangle|/\sum|F_o^2|$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

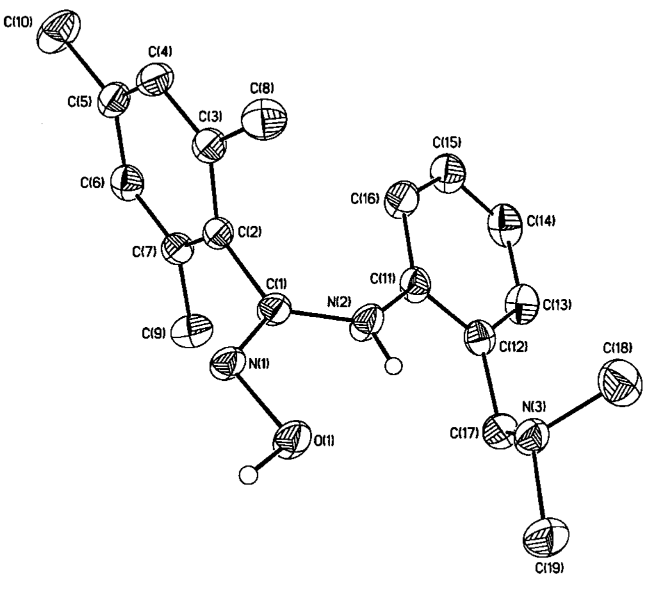


Figure 3. Molecular structure of H_2L (35% thermal ellipsoids). Hydrogen atoms, except H(1) and H(2), are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)−N(1), 1.287(2); N(1)−O(1), 1.429(2); C(1)−N(2), 1.364(3); C(1)−C(2), 1.493(3); N(2)−C(11), 1.408(3); N(1)−C(1)−C(2), 115.2(2); C(2)−C(1)−N(2), 122.4(2); N(1)−C(1)−N(2), 122.3(2); C(1)−N(2)−C(11), 129.8(2).

---

(10) Andrianov, V. G.; Eremeev, A. V. *J. Struct. Chem.* **1991**, *32*, 477 and references therein.

(11) Dondoni, A.; Gilli, G.; Sacerdoti, M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1036.

(12) Addition of a primary amine to a nitrile oxide is a common procedure for synthesizing N-monosubstituted amidoximes: Grundmann, C. In *The Chemistry of the Cyano Group*; Rapport, Z., Ed.; Interscience Publishers: New York, 1970; Chapter 14, pp 791−852.

(13) (a) Grundmann, C.; Dean, J. M. *J. Org. Chem.* **1965**, *30*, 2809. (b) Sindelar, K.; Valenta, V.; Holubek, J.; Matousova, O.; Protiva, M. *Collect. Czech. Chem. Commun.* **1990**, *55*, 282.

(14) Dondoni, A.; Barbaro, G.; Battaglia, A. *J. Org. Chem.* **1977**, *42*, 3372.

Scheme 1

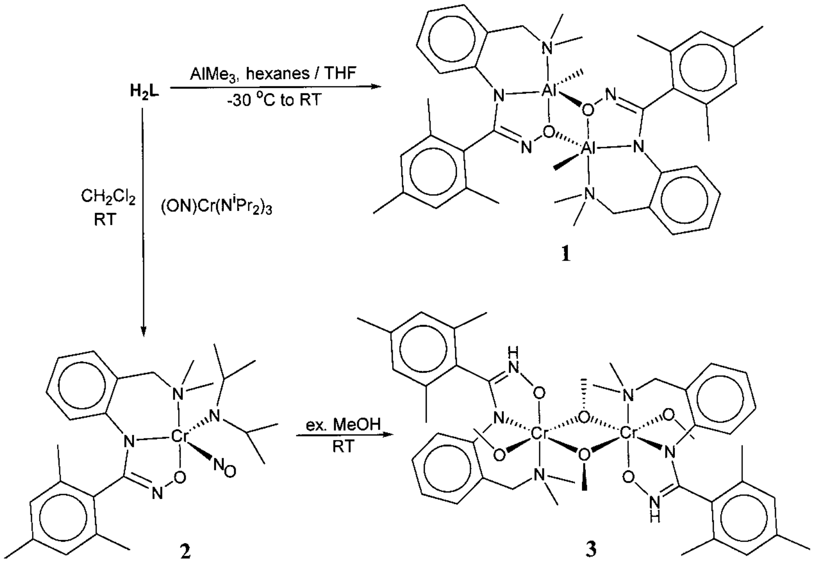


Table 2. Comparison of Selected Bond Distances (Å) and Angles (deg) for H_2L, **1**, and **3**

	C(1)−N(1)	C(1)−N(2)	N(1)−O(1)	C(1)−N(1)−O(1)
H_2L	1.287(2)	1.364(3)	1.431(2)	110.7(2)
1[a]	1.299(5)	1.377(5)	1.448(4)	108.2(3)
	1.306(6)	1.383(6)	1.440(4)	107.5(3)
	1.293(5)	1.380(5)	1.450(5)	108.0(3)
3	1.326(8)	1.332(8)	1.364(7)	118.4(6)

[a] Values for three independent molecules are listed.

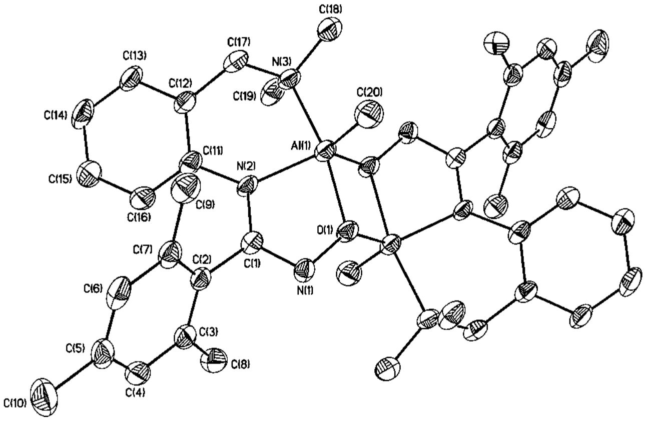


Figure 4. Molecular structure of $\mathbf{1}\cdot{}^{4}/_{3}C_6H_6$ (35% thermal ellipsoids). One of three independent molecules is shown. Hydrogen atoms and C_6H_6 molecules of crystallization are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−O(1), 1.843(3); Al(1)−O(1A), 1.903(3); Al(1)−N(2), 1.928(4); Al(1)−N(3), 2.042(4); Al(1)−C(20), 1.966(5); C(1)−N(1), 1.299(5); N(1)−O(1), 1.448(4); C(1)−N(2A), 1.377(5); C(1)−C(2), 1.505(6); N(2)−C(11), 1.410(3); O(1A)−Al(1)−N(3), 158.9(2); O(1)−Al(1)−C(20), 116.0(2); O(1)−Al(1)−N(2), 122.9(2); N(2)−Al(1)−C(20), 118.5(2); N(1)−C(1)−C(2), 112.7(4); C(2)−C(1)−N(2A), 126.0(4); N(1)−C(1)−N(2A), 121.2(4); C(1A)−N(2)−C(11), 120.2(4).

Metal Complexes Derived from H_2L. To test the ligating ability of L^{2-}, $AlMe_3$ was treated with 1 equiv of H_2L at −30 °C (Scheme 1). A vigorous gas evolution was observed. The product $(MeAlL)_2$ (**1**), isolated in 77% yield, was shown by X-ray crystallography to be a dimeric organoaluminum species (Table 1, Figure 4). As anticipated, protonolysis of two methyl groups of $AlMe_3$ generated the formally dianionic ligand L^{2-}, bound to the aluminum via the oximato oxygen and the amido and amino nitrogens. In addition, the oximato O atoms serve to link the two monomeric units together. Compound **1** crystallizes in the space group $P\bar{1}$. The centers of three crystallographically independent dimers are located on special positions (inversion centers), resulting in $Z = 6$. The structural parameters of these dimers are essentially identical. For **1**, irregular five-coordination at aluminum is in evidence. As expected, the metal−amido bond length (Al(1)−N(2)) is 0.114 Å shorter than the metal−amino distance (Al(1)−N(3)). Table 2 shows that the bond distances and angles within the amidoximato ligand in **1** are quite similar to the corresponding parameters obtained for the parent amidoxime H_2L.

From Figure 4, it is apparent that every carbon atom of a monomeric portion of **1** should have a unique magnetic environment. Accordingly, 19 resonances were observed in the ^{13}C NMR spectrum of **1**. The peak due to the AlCH_3 carbon was not detected, presumably because of $^{13}C-^{27}Al$ coupling. Interestingly, the chemical shift of C(1) for **1** occurs ca. 12.5 ppm downfield with respect to that for H_2L, while the $\nu_{C=N}$ stretching vibration for **1** is 11 cm^{-1} lower in energy than $\nu_{C=N}$ observed for H_2L in the same solvent (THF).

Facile replacement of the amido ligands from $(ON)Cr(N^iPr_2)_3$[17,18a,b] and $NCr(N^iPr_2)_3$[19] by action of protic reagents has been documented. For example, reactions of $(ON)Cr(N^iPr_2)_3$ with 2 equiv of $PhCO_2H$ or ^tBuOH afforded $(ON)Cr(N^iPr_2)(O_2CPh)_2$[17] or $(ON)Cr(N^iPr_2)(O^tBu)_2$,[18a,c] respectively. Similarly, treatment of orange-red $(ON)Cr(N^iPr_2)_3$ with 1 equiv of H_2L produced dark maroon, diamagnetic $(ON)Cr(N^iPr_2)(\eta^3\text{-}L)$ (**2**) in 87% yield (Scheme 1). The IR spectrum of **2** in CH_2Cl_2 exhibits a very strong band at 1677 cm^{-1}, corresponding to the

---

(15) Buzykin, B. A.; Dokuchaev, A. S.; Kharitonova, O. A. *Russ. Chem. Bull.* **1995**, *44*, 1456.

(16) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(17) (a) Jandciu, E. W.; Kuzelka, J.; Legzdins, P.; Rettig, S. J.; Smith, K. M. *Organometallics* **1999**, *18*, 3569. (b) Kuzelka, J.; Legzdins, P.; Rettig, S. J.; Smith, K. M. *Organometallics* **1997**, *16*, 3569.

(18) (a) Bradley, D. C.; Newing, C. W. *J. Chem. Soc., Chem. Commun.* **1970**, 219. (b) Bradley, D. C.; Newing, C. W.; Chisholm, M. H.; Kelly, R. L.; Haitko, D. A.; Little, D.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1980**, *19*, 3010. (c) Cummins, C. C. *Prog. Inorg. Chem.* **1998**, *47*, 685.

(19) (a) Odom, A. L.; Cummins, C. C. *Polyhedron* **1998**, *17*, 675. (b) Odom, A. L.; Cummins, C. C. *Organometallics* **1996**, *15*, 898.

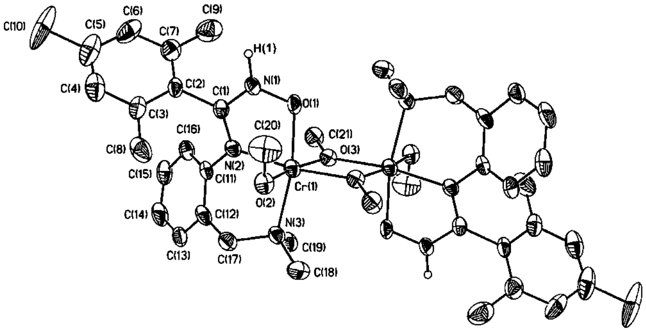


Figure 5. Molecular structure of **3**·MeOH (35% thermal ellipsoids). Hydrogen atoms, except H(1), and MeOH of crystallization are omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−O(1), 1.953(5); Cr(1)−O(2), 1.946(5); Cr(1)−O(3), 1.988(5); Cr(1)−O(3A), 1.982(4); Cr(1)−N(2), 2.065(5); Cr(1)−N(3), 2.194(6); C(1)−N(1), 1.326(8); N(1)−O(1), 1.364(7); C(1)−N(2), 1.332(8); C(1)−C(2), 1.500(10); N(2)−C(11), 1.411(8); O(2)−C(20), 1.426; O(3)−C(21), 1.414(8); O(1)−Cr(1)−N(3), 167.4(2); O(2)−Cr(1)−O(3), 170.2(2); N(2)−Cr(1)−N(3A), 170.7(2); N(1)−C(1)−C(2), 116.3(7); C(2)−C(1)−N(2), 127.3(6); N(1)−C(1)−N(2), 116.3(7); C(1)−N(2)−C(11), 120.8(6); C(1)−N(2)−Cr(1), 110.0(4).

stretching vibration of the linear nitrosyl ligand. The energy of this vibration is 36 cm^{-1} higher than ν_{NO} observed[18a] for $(ON)Cr(N^iPr_2)_3$ in the same solvent. This is in accord with the amidoximato ligand L^{2-} being a poorer π donor as compared to two diisopropylamido groups. Appreciable differences in the ^1H and ^{13}C chemical shifts for two NMe_2 methyl groups suggest that the nitrogen atom of the CH_2NMe_2 arm is bound to the metal. As in **1**, the metal center in **2** is chiral, and every carbon atom is unique in terms of its magnetic environment. Consequently, 25 peaks were found in the ^{13}C NMR spectrum of **2**. The chemical shift of the C(1) carbon is about 5.5 ppm downfield from that of the corresponding value determined for free H_2L. Unfortunately, numerous attempts to grow X-ray quality single crystals of **2** failed. Therefore, structural characterization of a derivative of **2** was sought.

Addition of excess dry methanol to a sample of **2** produced a green, paramagnetic precipitate $[Cr(LH)(OMe)(\mu\text{-}OMe)]_2$ (**3**)(Scheme 1). When the reaction was conducted in CD_3OD, $DN^i\text{-}Pr_2$ was the only diamagnetic product detected in solution by ^1H NMR. The IR spectrum of **3**, dissolved in toluene, was found not to exhibit any strong bands attributable to ν_{NO} of the nitrosyl ligand. It is worth mentioning that Legzdins' $(ON)Cr(N^iPr_2)(O_2CPh)_2$ reacts slowly with $PhCO_2H$ to give an unknown "green, paramagnetic solid whose IR spectrum (CH_2Cl_2) is devoid of infrared bands in the nitrosyl-stretching region."[17b]

X-ray crystallographic characterization was essential for elucidating the nature of **3** (Table 1). The molecular structure of **3** is shown in Figure 5. It is comprised of two six-coordinate Cr centers linked by two methoxy bridges. The dimer lies on an inversion center, so only half of the molecule is crystallographically independent. The Cr_2O_2 core is planar with the Cr(1)···Cr(1A) distance of 3.132(1) Å outside of the bonding range.[20] Since the amidoximato ligand appeared to be intact, the presence of two methoxy groups per chromium was initially surprising. The Cr(1)−O(2), Cr(1)−O(3) and Cr(1)−O(3A) distances are typical[21] for Cr(III) bonds with terminal and bridging alkoxides, respectively, so coordination of a neutral MeOH molecule was safely ruled out. However, during the solution and refinement procedure, a hydrogen atom H(1) was located within ca. 1 Å from the oximato nitrogen N(1). This nicely explains a band at 3341 cm^{-1} (ν_{N-H}) in the IR spectrum of **3.** Thus, treatment of **2** with MeOH resulted in protonolysis of the diisopropylamido group accompanied by introduction of the methoxy ligand, oxidative loss of neutral NO, and O−H cleavage of another methanol molecule by means of protonation of the oximato nitrogen. The latter process provided the second methoxy ligand. While unusual, the structural motif (η^3-HL)M, found in **3**, is not unprecedented. Indeed, three crystallographically characterized related examples, all obtained unexpectedly and containing bidentate ligand $[-HNC(Ph)NHO-]^-$, have been described.[9b,22] Several complexes having N-protonated η^1 oximato fragments have been reported as well.[23] Bonding characteristics within HL in **3** deserve special attention. The C(1)−N(1) and C(1)−N(2) distances are identical within their estimated standard deviations and are between the values expected for C−N single and double bonds.[16] This is in sharp contrast to what was found for free H_2L and **1** (see Table 2). In addition, the N(1)−O(1) bond in **3** is considerably shorter than these distances in H_2L and **1** (Table 2). The above facts suggest a full delocalization of the π electron density over the entire amidoximato ONCN moiety in **3**. It is worth mentioning that protonation of the oximato nitrogen causes an appreciable expansion of the C−N−O angle with respect to the corresponding values obtained for the free amidoxime H_2L and **1** (Table 2).

Since the ligand $[HL]^-$ is monoanionic, the formal oxidation state of the chromium atoms in **3** should be +3. The effective magnetic moment of **3** in benzene solution is 3.5 μ_B per chromium at room temperature. This value is similar to those found for a large family[20] of weakly antiferromagnetically coupled, edge-sharing, bioctahedral, alkoxy-bridged chromium(III) dimers, such as $[(acac)_2Cr(OMe)]_2$.[24]

Summary and Conclusions

The high-yield, multigram preparation of the new amidoxime H_2L possessing a pendant amino functionality was accomplished by reaction of equimolar amounts of the appropriate nitrile oxide and primary amine. Its conjugate base, L^{2-}, was shown to function as a chelating, dianionic ligand. Syntheses of the aluminum and chromium compounds **1** and **2** represent a potentially general strategy for accessing the rarely encountered coordination of amidoximates through both oximato O and amido N atoms. Such binding was facilitated by incorporation of the amino arm, which provided a six-membered metallacycle upon complexation. Interaction of **2** with excess methanol resulted in complex **3**, containing the monoanionic amidoximato ligand $[HL]^-$ protonated at its oximato nitrogen. While unexpected, the latter reaction is in accord with the well-established propensity of oximes to bind to Lewis acids (e.g., metal ions) via the oxime nitrogen.[1,3b]

---

(20) (a) Chisholm, M. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, pp 335−364. (b) Larkworthy, L. F.; Nolan, K. B.; O'Brian, P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 3, pp 699−969.

(21) *International Tables for Crystallography*, 2nd ed.; Prince, E., Wilson, A. J. C., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1999; Vol. C.

(22) (a) Malatesta, L.; La Monica, G.; Manassero, M.; Sansoni, M. *Gazz. Chim. Ital.* **1980**, *110*, 113.

(23) (a) Burdinski, D.; Birkelbach, F.; Gerdan, M.; Trautwein, A. X.; Wieghart, K. *Chem. Commun.* **1995**, 963. (b) Proust, A.; Gouzerh, P.; Robert, F. *J. Chem. Soc., Dalton Trans.* **1994**, *819*, 825. (c) Roh, S.-G.; Proust, A.; Gouzerh, P.; Robert, P. *Chem. Commun.* **1993**, 836. (d) Witte, E. G.; Schwochau, K. S.; Henkel, G.; Krebs, B. *Inorg. Chim. Acta* **1984**, *94*, 323.

(24) (a) Fischer, H. R.; Glerup, J.; Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1982**, *21*, 3063. (b) Fischer, H. R.; Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1984**, *23*, 4755.

Experimental Section

General Procedures and Starting Materials. Unless stated otherwise, all operations were performed under an atmosphere of purified nitrogen in a Vacuum Atmospheres drybox or under an atmosphere of 99.5% argon using conventional Schlenk techniques. Solvents, including deuterated solvents, were freed of impurities by standard procedures and stored over 4-Å molecular sieves under nitrogen. Modified literature procedures were employed to prepare mesitylnitrile oxide[12a] and 2-[(dimethylamino)methyl]aniline[12b] (see Supporting Information). The complex (ON)Cr(N^iPr_2)$_3$ was synthesized according to a published protocol.[18a]

Solution infrared spectra were recorded on a Bio-Rad FTS 135 spectrometer with samples sealed in 0.1-mm, gastight, NaCl cells. NMR samples were sealed under nitrogen into 5-mm tubes and were analyzed on Varian VXR-500, Varian XL-300, or Varian Unity-300 spectrometers. ^{1}H and ^{13}C chemical shifts are given iin ppm with reference to residual ^{1}H and ^{13}C solvent resonances relative to TMS. Assignments of ^{1}H and ^{13}C peaks were facilitated by acquiring COSY, HMQC, and DEPT spectra and by simulating ^{1}H and ^{13}C NMR patterns with the help of ADC−HNMR and ACD−CNMR software (Version 4.57, Advanced Chemistry Development Inc., Toronto, Ontario, Canada). The numbering scheme used for the NMR assignments is identical to those in Figures 3−5. Solution magnetic measurements were performed using the Evans method.[25] The diamagnetic correction applied to the molar susceptibility of **3** (-250×10^{-6} cm^3 mol^{-1} for the empirical formula of **3**) was calculated using Pascal's constants.[26] Melting points are uncorrected, and they were determined for samples in capillaries sealed under nitrogen on a MEL-TEMP II (Laboratory Devices) apparatus. C, H, and N analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany).

Synthesis of H_2L. This procedure did not require anaerobic conditions. Solid 2-[(dimethylamino)methyl]aniline (42.9 mmol, 6.45 g) was added all at once to an efficiently stirred solution of mesitylnitrile oxide (40.9 mmol, 6.60 g) in 200 mL of warm (ca. 40 °C) methanol. The resulting colorless mixture was refluxed for 1 h. After being cooled to room temperature, the pale yellow solution was filtered. All but 30 mL of methanol was slowly removed in vacuo to afford a colorless microcrystalline precipitate. The solid was filtered off, washed with cold (0 °C) light petroleum ether (4 × 20 mL) until the washings were colorless, and dried under vacuum to provide 6.70 g of pure H_2L. The filtrate, combined with the washings, was concentrated to about 10 mL and worked up as above to give an additional 3.99 g of H_2L. Yield: 84% (34.3 mmol, 10.69 g). mp: 170−172 °C dec. Anal. Calcd for $C_{19}H_{25}N_3O$: C, 73.28; H, 8.09; N, 13.49. Found: C, 73.37; H, 7.93; N, 13.58. IR (THF, cm^{-1}) $\nu_{O-H,N-H}$: 3353 (m, vbr); $\nu_{C=N}$: 1622 (s). ^{1}H NMR (300 MHz, C_6D_6, 22 °C): δ 2.00 (s, 6H, $H^{8,9}$), 2.06 (s, 3H, H^{10}), 2.29 (s, 6H, $H^{18,19}$), 3.30 (s, 2H, H^{17}), 6.44 (dd, 1H, $^3J_{H-H} = 8.0$ Hz, $^4J_{H-H} = 1.0$ Hz, H^{16}), 6.61 (td, 1H, $^3J_{H-H} = 7.2$ Hz, $^4J_{H-H} = 1.0$ Hz, H^{14}), 6.65 (s, 2H, $H^{4,6}$), 6.70 (td, 1H, $^3J_{H-H} = 8.0$ Hz, $^4J_{H-H} = 1.8$ Hz, H^{15}), 6.85 (dd, 1H, $^3J_{H-H} = 7.2$ Hz, $^4J_{H-H} = 1.8$ Hz, H^{13}), 10.54 (s, 1H, O*H*), 10.64 (s, br, 1H, N*H*). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 22 °C): δ 20.23 ($C^{8,9}$), 21.57 (C^{10}), 44.80 ($C^{18,19}$), 63.76 (C^{17}), 119.72 (C^{16}), 121.81 (C^{14}), 128.52, 128.55 (C^{13}, C^{15}), 129.13 ($C^{4,6}$), 129.99, 130.47 (C^2, C^{12}), 138.45 ($C^{3,7}$), 138.85 (C^5), 141.05 (C^{11}), 149.95 (C^1).

Synthesis of (MeAlL)$_2$ (1). A cold (−30 °C) solution of H_2L (6.260 mmol, 1.950 g) in 12 mL of THF was added dropwise to a well-stirred, thawing 2.0 M solution of $AlMe_3$ (6.40 mmol, 3.20 mL) in hexanes. Vigorous gas evolution was observed. The mixture was warmed to room temperature. After being stirred for 3 h, the mixture was diluted with 15 mL of THF to dissolve practically all white precipitate deposited during the reaction. The resulting pale yellow solution was filtered. Addition of pentane (20 mL) to the filtrate, concentrated to about 5 mL, afforded a white precipitate of **1**. The solid was filtered off, washed with pentane (3 × 10 mL), and dried under vacuum (10^{-2} Torr) for 24 h. Concentration of the filtrate and precipitation with pentane provided another crop of pure **1**. Yield: 77% (4.82 mmol, 1.694 g). mp: 294−296 °C dec. Anal. Calcd for $C_{20}H_{26}N_3AlO$: C, 68.36; H, 7.46; N, 11.96. Found: C, 68.49; H, 7.36; N, 12.07. IR (THF, cm^{-1}) $\nu_{C=N}$: 1611 (m). ^{1}H NMR (300 MHz, C_6D_6, 22 °C): δ −0.29 (s, 3H, AlC*H*$_3$), 2.08 (s, 3H, H^{10}), 2.35 (s, 6H, $H^{8,9}$), 2.44 (s, 3H, H^{18or19}), 2.52 (s, 3H, H^{19or18}), 3.00 (d, 1H, $^2J_{H-H} = 12.6$ Hz, H^{17}), 3.62 (d, 1H, $^2J_{H-H} = 12.6$ Hz, $H^{17'}$), 6.58 (td, 1H, $^3J_{H-H} = 7.2$ Hz, $^4J_{H-H} = 1.2$ Hz, H^{14}), 6.66 (s, 1H, H^{4or6}), 6.69 (dd, 1H, $^3J_{H-H} = 7.2$ Hz, $^4J_{H-H} = 1.8$ Hz, H^{16}), 6.73 (dd, 1H, $^3J_{H-H} = 8.0$ Hz, $^4J_{H-H} = 1.2$ Hz, H^{13}), 6.76 (s, 1H, H^{6or4}), 6.81 (td, 1H, $^3J_{H-H} = 8.0$ Hz, $^4J_{H-H} = 1.8$ Hz, H^{15}). ^{13}C{^{1}H} NMR (125.8 MHz, C_5D_5N, 22 °C): δ 21.16, 21.63, 21.67 (C^8, C^9, C^{10}), 45.70, 46.67 (C^{18}, C^{19}), 64.26 (C^{17}), 120.60 (C^{14}), 121.79 (C^{16}), 129.31, 129.40, 129.56, 131.04 (C^4, C^6, C^{13}, C^{15}), 125.30, 132.193, 137.75, 137.98, 138.30, (C^2, C^3, C^5, C^7, C^{12}), 146.63 (C^{11}), 162.39 (C^1).

Synthesis of Cr(NO)(N^iPr_2)L (2). A colorless solution of H_2L (5.587 mmol, 1.740 g) in 20 mL of CH_2Cl_2 was added to an orange-red solution of Cr(NO)(N^iPr_2)$_3$ (5.578 mmol, 2.134 g) in 40 mL of CH_2Cl_2 at room temperature. The mixture acquired a dark maroon color and was stirred for 24 h. Following filtration, all solvent was evaporated, and the residue was dried under vacuum to remove HN^iPr_2. Trituration of the residue in 50 mL of pentane resulted in a dark maroon, almost black solid. The latter was filtered off, washed with 70 mL of pentane, and dried in vacuo to afford analytically pure **2** as a free flowing, sparkling powder. Yield: 87% (4.862 mmol, 2.400 g). mp: 194−197 °C dec. Anal. Calcd for $C_{25}H_{37}N_5CrO_2$: C, 61.08; H, 7.59; N, 14.25. Found: C, 60.92; H, 7.65; N, 14.17. IR (CH_2Cl_2, cm^{-1}) ν_{NO}: 1677 (vs). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 0.59 (d, 3H, $^3J_{H-H} = 6.3$ Hz, C*H*$_3$, N^iPr_2), 0.96 (d, 3H, $^3J_{H-H} = 6.3$ Hz, C*H*$_3$, N^iPr_2), 1.56 (d, 3H, $^3J_{H-H} = 6.3$ Hz, C*H*$_3$, N^iPr_2), 1.59 (s, 3H, H^{8or9}), 1.72 (d, 3H, $^3J_{H-H} = 6.3$ Hz, C*H*$_3$, N^iPr_2), 2.25 (s, 3H, H^{10}), 2.34 (s, 6H, H^{18or19}), 2.53 (s, 3H, H^{9or8}), 3.04 (s, 3H, H^{19or18}), 3.08 (d, 1H, $^2J_{H-H} = 12.0$ Hz, H^{17}), 3.73 (d, 1H, $^2J_{H-H} = 12.0$ Hz, $H^{17'}$), 4.10 (sept, 1H, $^3J_{H-H} = 6.3$ Hz, C*H*, N^iPr_2), 5.24 (sept, 1H, $^3J_{H-H} = 6.3$ Hz, C*H*, N^iPr_2), 6.37 (d, 1H, $^3J_{H-H} = 7.8$ Hz, H^{16}), 6.59 (s, 1H, H^{4or6}), 6.89 (t, 1H, $^3J_{H-H} = 6.9$ Hz, H^{14}), 6.95 (s, 1H, H^{6or4}), 7.06 (t, 1H, $^3J_{H-H} = 7.5$ Hz, H^{15}), 7.17 (d, 1H, $^3J_{H-H} = 6.9$ Hz, H^{13}). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 22 °C): δ 19.75 (C^{8or9}), 21.39 (C^{10}), 21.82 (C^{11}), 21.88 (*C*H$_3$, N^iPr_2), 23.20 (*C*H$_3$, N^iPr_2), 27.40 (*C*H$_3$, N^iPr_2), 29.65 (*C*H$_3$, N^iPr_2), 50.97, 54.18 (C^{18}, C^{19}), 63.04 (*C*H, N^iPr_2), 67.95 (C^{17}), 68.39 (*C*H, N^iPr_2), 122.15 (C^{16}), 122.44 (C^{14}), 128.10, 128.34 (C^4, C^6), 129.81 (C^{15}), 130.17 (C^{13}), 127.61, 129.42, 136.90, 137.65, 138.37 (C^2, C^3, C^5, C^7, C^{12}), 146.50 (C^{11}), 155.44 (C^1).

Synthesis of [Cr(LH)(OMe)(μ-OMe)]$_2$ (3). Dry methanol (15 mL) was added to solid **2** (1.852 mmol, 0.930 g) under argon to give a dark maroon solution. The color of the reaction mixture faded gradually, and a green microcrystalline precipitate started to form within 20 min after the addition of MeOH. The mixture was stirred for 10 h. All volatiles were then removed in vacuo. The green residue was suspended in pentane, filtered off, washed with pentane (4 × 10 mL), and dried under vacuum to afford **3** as a free-flowing, sparkling green powder. Yield: 75% (1.411 mmol, 0.599 g). mp: 192 °C dec (darkens at ca. 95 °C). Anal. Calcd for $C_{21}H_{30}N_3CrO_3$: C, 59.42; H, 7.12; N, 9.90. Found: C, 59.60; H, 7.20; N, 10.25. IR ($CH_3C_6H_5$, cm^{-1}) ν_{N-H}: 3341 (m); μ_{eff} (293 K) = 3.5 μ_B (solution in C_6D_6−($Me_3Si)_2O$).

X-ray Crystallographic Characterization of H_2L, 1·$^4/_3C_6H_6$, and 3·MeOH. X-ray quality crystals of H_2L were grown from a concentrated solution of this compound in methanol at 4 °C. Slow evaporation of a benzene solution of **1** at room temperature provided single crystals of **1**·$^4/_3C_6H_6$ suitable for X-ray diffraction analysis. Single crystals of **3**·MeOH were obtained by adding dry methanol to a sample of **2** and keeping the resulting mixture under an inert atmosphere for 2 days without stirring. A selected crystal was coated with Paratron N oil (Exxon), attached to a glass fiber, and mounted on a Siemens SMART Platform CCD diffractometer for a data collection (Mo Kα radiation with $\lambda = 0.710\,73$ Å was employed). Space groups were determined based on systematic absences and intensity statistics. Successful direct-methods solutions were calculated, which provided most non-hydrogen atoms from the *E*-maps. Several full-matrix least-squares difference

---

(25) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Crawford, T. H.; Swanson, J. *J. Chem. Educ.* **1971**, *48*, 382. (c) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

(26) (a) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993. (b) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: New York, 1968. (c) König, E. *Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik* (Numerical Data and Functional Relationships in Science and Technology), 6th ed.; Springer-Verlag: Berlin, 1966; Vol. 2, p 16.

Fourier cycles were performed to locate the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of H_2L and H(1) of **3**·MeOH were directly located in the appropriate difference maps and refined isotropically. Other hydrogen atoms were placed in ideal positions and refined as riding atoms with individual or group isotropic displacement parameters. For **3**·MeOH, four hydrogen atoms of the disordered MeOH molecule of crystallization were neglected in the refinement procedure. Semiempirical absorption correction from psi scans was applied to all data. Calculations were performed using the SHELXTL Version 5.0 suite of programs (Sheldrick, G. M. *SHELXTL*, Version 5.0; Siemens Industrial Automation, Inc.: Madison, WI, 1995). Crystal data, data collection, solution, and refinement information for H_2L, **1**·$^4/_3C_6H_6$, and **3**·MeOH is provided in Table 1. Additional crystallographic details can be found in the Supporting Information.

Acknowledgment. For financial support of this work, the authors are grateful to the Union Carbide Corporation. The authors thank Dr. Jessica Cook and Dr. Daniel J. Mindiola for helpful discussions.

Supporting Information Available: Improved syntheses of and spectroscopic data for mesitylnitrile oxide and 2-[(dimethylamino)-methyl]aniline, crystallographic data for the X-ray structures of H_2L, **1**·$^4/_3C_6H_6$, and **3**·MeOH in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0100370